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(54) Title: CARBOHYDRATE GLUE (57) Abstract Fructans, in particular inulin, and derivatives thereof can be used as a glue. Preferably, a 10-80 % solution or dispersion of inulin or reduced or oxidised inulin in water or a hot 40-95 % solution or dispersion of inulin in glycol or glycerol is employed. The fructan, in particular, has a chain length of 4-20. The use is primarily directed at gluing paper, paper products, plastic products, wood or wood products, textile and cellulose products, with the advantage that less solvent needs to be used and evaporated.		

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Carbohydrate glue

The invention relates to the use of carbohydrates as a glue.

For many glue applications the use of natural raw materials is desirable. Glues from natural raw materials are currently mostly based on starch. Starch is a polymer of glucose units which are linked to one another cis-1-4 and/or cis-1-6. These starch
5 glues are much used in the paper industry to glue paper and cardboard.

For this application, solutions of starch are used which are able to contain at most from 5 to 10% dry weight of starch, since starch dissolves poorly in water. Consequently, the drying process after gluing is an expensive factor in the production process, since approximately from 90 to 95% of the applied glue consists of water
10 which for the greater part must be removed at great cost in terms of energy. To alleviate this problem, oxidised starches are currently also used, which are more soluble in water, as a result of which the glues based on them can have a higher solids content. A drawback of this solution is that a large number of process steps are required to arrive
15 at the desired compound.

It is therefore an object of the invention to develop a type of glue which is based on natural raw materials and which can be employed at higher concentrations than starch, preferably without the necessary involvement of additional process steps. At the same time, the natural raw material must be obtainable relatively inexpensively.

20 It was found that a concentrated solution or dispersion of fructans such as inulin, or derivatives thereof such as partially hydrolysed inulin or fructo-oligosaccharides, reduced derivatives, oxidised derivatives or other derivatives thereof in water or other solvents is eminently suitable as a glue. The invention therefore relates to the use of fructans and/or derivatives thereof as a glue.

25 The fructan inulin is an entirely or largely linear polysaccharide, which is composed of 2,1- β -linked anhydrofructose units usually having a terminal glucose unit and sometimes a β -2,6 side chain. It is obtained, for example, from Jerusalem artichoke, artichoke, chicory, dahlia and dandelion. Fructans can also be obtained by enzymatic synthesis. Inulin of vegetable origin has a chain length (DP) of 3-30 or more, sometimes
30 up to 80. Preferably inulin having an average chain length of 4-20, in particular of 6-11 monosaccharide units is used. Instead of inulin it is also possible to use another

polysaccharide which is largely composed of anhydrofructose units, such as levan (a branched 2,6-fructan).

The major advantage of the use of inulin and derivatives thereof as a glue is that much less solvent is required to apply the correct amount to, for example, paper or cardboard. As a result, less solvent has to be evaporated, so that the duration of the process and the process costs can be considerably reduced. A second advantage is that, in contrast to starch, no chemical modification is required for obtaining the desired high concentration, even with higher chain lengths.

Preferably, a solution or dispersion of inulin in water with a concentration of 10–80 wt.% is used. In particular, a solution or dispersion of 20–50 wt.% is used. The inulin solutions or dispersions can be used as a glue at ambient temperature, but preferably a slightly elevated temperature is employed, in particular 30–70°C.

Instead of inulin it is also possible to use derivatives of inulin, such as hydrolysed, oxidised, reduced, carboxyalkylated, esterified and etherified and other chemical derivatives. Examples of oxidised derivatives are dialdehyde inulin and carboxylated inulin.

Dialdehyde inulin is obtained from inulin by oxidation with an oxidant which oxidises primarily or exclusively vicinal diol functions, such as periodate and the like. According to the invention it is not necessary, when dialdehyde inulin is used, for all the vicinal diol functions, i.e. all the fructan rings, to be oxidised. In general, 0.1–100% of the diol functions can be oxidised. In particular, a dialdehyde inulin can be used of which 1–60%, especially 1–30% of the vicinal diol functions have been oxidised. Derivatives wherein some of the aldehyde functions have further been oxidised to carboxylic acid groups, and derivatives wherein the dialdehyde functions have been disproportionated into a carboxylic acid and a primary alcohol or have undergone further conversion in some other way are likewise usable.

Carboxylated inulin can be obtained from inulin in a known manner, for example by a two-step oxidation with periodate to the dialdehyde, and chlorite to the dicarboxylic acid to produce dicarboxyinulin. Dicarboxyinulin can also be obtained by means of the method according to WO 91/17189 by single-step oxidation with a hypohalite. Another suitable method of producing carboxylated inulin is the oxidation of inulin with hydrogen peroxide in the presence of alkali metal halides or transition metal

salts. In the case of the carboxylated inulin derivatives it is likewise unnecessary for all the diol functions to have been oxidised to carboxylic acids. In general, a carboxylated inulin can be used, in which 0.1–100% of the anhydrofructose units have been oxidised, and in particular a carboxylated inulin in which 1–60%, especially 1–30% of the diol functions have been oxidised.

Oxidised inulin derivatives in which the 6-hydroxyl function of the anhydrofructose units has been oxidised entirely or in part to a carboxylic acid group, optionally in conjunction with a partial oxidation of the vicinal diol function to a dialdehyde or carboxylated acid, can likewise be used according to the invention.

Reduced inulin, i.e. an inulin wherein a reducing end has been hydrogenated, is also suitable for use as a glue. Reducing agents capable of producing reduced inulin include molecular hydrogen in the presence of a suitable catalyst such as Raney nickel, and hydride donors such as sodium borohydride. Reduction can also be performed by electrochemical means, e.g. using an amalgamated lead electrode in an alkaline or neutral medium, or, alternatively, using a graphite electrode in dilute sulphuric or other acid.

The solvent to be used for the solution or dispersion of inulin or its derivative can be water, alcohols and polyols, and other polar solvents such as amides, nitriles, ketones although these are less preferred than the alcohols and polyols, and water. Suitable alcohols include C₁–C₆ alkanols. Suitable polyols include ethylene glycol, propylene glycol, di- or triethylene glycol, monoalkyl ethers and monoester of a glycol and glycerol. Most preferred at low temperatures is water.

Particularly good results are also obtained, surprisingly, with so-called "hot melts" of fructans. This term refers to concentrated solutions or dispersions of the fructan in a solvent with a temperature of 60–160°C, in particular 80–140°C. These hot melts can be prepared by mixing the fructan or derivative and the solvent and optional additives at 80–160°C, in particular at 100–140°C, especially at 110–120°C, if necessary with stirring or kneading. At temperatures above 100°C and atmospheric pressure preference is given to the use of a high-boiling solvent such as the polyols referred to above or a mixture thereof, in particular glycerol. The concentrated solution or dispersion contains 10–99 wt.%, preferably 40–95 wt.%, in particular 60–90 wt.% of fructan, in particular inulin. The concentrated solution or dispersion may also contain further

additives such as plasticisers, fillers, binders and the like, for example other carbohydrates such as starch, lactose, sucrose, proteins such as gluten, soy protein or whey protein, fats, emulsifiers, urea, salts such as lime, and the like. Preferably the amount of such additives is less than the amount of fructan or derivative thereof.

5 The invention also relates to solutions and dispersions of 10–99 wt.%, preferably 40–95 wt.%, in particular 60–90 wt.%, of fructan in a polyol, said solutions and dispersions being usable in the above-mentioned "hot melts".

 The solutions or dispersions of inulin or inulin derivatives can be employed for various purposes. In particular, these solutions or dispersions are employed for gluing
10 paper and paper goods such as cardboard, or for gluing plastic parts, wood or products into which wood has been incorporated. The "hot melts" can be used especially in the paper industry and the packaging industry, in particular for gluing together two or more objects, at least one of which is paper, a paper-containing product, wallpaper, textile, a plastic product, wood, a wood-containing product or a cellulose-containing product.
15 The solutions, dispersions and especially "hot melts" can also be used as a sealing material or on labels.

Example 1

Preparation of inulin glue:

20 To an amount of water, such an amount of inulin is added at 80°C that a solution having a solids content of 30% is obtained. The solution is then cooled to 50°C and is ready for use.

Example 2

Preparation of dialdehyde inulin:

25 To a stirred solution of inulin in water (5–10 wt.%) a calculated amount of sodium metaperiodate is added until the desired degree of oxidation is achieved, for example 50%. Any remaining sodium metaperiodate and reaction products thereof are removed by precipitation from ethanol, and the oxidised inulin is then isolated, for example by means of the solution being concentrated.

Example 3

30 Preparation of carboxylated inulin:

100 g of inulin, isolated from chicory, with an average DP of approximately 9,

are dissolved in 3 l of water. To this 3 g of sodium chloride are added. The system is brought to 50°C. To this mixture, 180 g of hydrogen peroxide (35% w/v) are added over one hour. The reaction mixture is kept at pH 5. After 24 hours the reaction mixture is boiled down. The carboxylated inulin is obtained in a yield of more than 90%.

5 Example 4

An inulin solution obtained according to Example 1, wherein Frutafit® (a designation of commercially available inulin from chicory having an average DP of approximately 10 monosaccharide units) had been employed, was used to glue together sheets of paper of copying quality. The gluing area is 375 mm² and the thickness of the glue layer is 0.01–0.15 mm. The surfaces glued together are stored in a conditioned environment of 20°C and 60% relative humidity. Once the weight of the glued sheet no longer changes, tensile strengths are measured.

Table 1: Peeling experiments paper on paper

	Dry substance used	% (w/w)	Tensile strength (N/m ²)
15	standard Frutafit®	20	1.1
	"	40	3–4
	"	60	5–6
	instant Frutafit®	20	1.6
	"	40	4–5
20	"	60	5
	sucrose	20	1.6
	"	60	3–4
	maltodextrin	20	4–5
	"	60	5–6
25	starch	5	5–6
	"	10	6–7
	"	20	6–7
	technicol	--	7

Technicol is a commercially available glue based on synthetic components.

The tensile strength of the glued paper was measured in peeling tests involving a tensile testing machine. The results of these are shown in Table 1, together with those of some other carbohydrates.

It can be seen from the results in Table 1 that the gluing quality of inulin is comparable to that of starch. Owing to the higher concentrations of the inulin solutions, the drying time and the energy required for drying are reduced.

Table 2: Results of sheet-on-sheet tensile tests

	Dry substance used	% (w/w)	Shear stress (N/m ²)
10	standard Frutafit®	20	1.0
	"	30	1.8
	"	40	2.0
	"	50	2.3
	"	60	1.9
15	instant Frutafit®	20	1.1
	"	30	2.2
	"	40	1.9
	"	50	1.8
	"	60	1.4
20	maltodextrin	20	0.8
	"	30	0.8
	"	40	0.7
	"	50	0.9
	"	60	0.5
25	sucrose	20	0.2
	"	30	0.2
	"	40	0.7
	"	50	0.8
	"	60	0.9
30	starch	5	2.1
	"	10	1.1
	"	20	0.5
	technicol	--	3.3

The gluing quality of this inulin solution when used on polyethylene terephthalate sheets for copying purposes was likewise determined. The results of these are shown in Table 2.

5 In this application the inulin glue is likewise found to give a result comparable to that of starch. In particular, the inulin solutions having a high solids content compared to starch exhibit a comparable to better result. Here too the high concentration has a beneficial effect on the process costs as a result of shorter drying times and a lower energy requirement.

Example 5

10 100 g of glycerol are introduced into a kneader (Haake Rheocord® 90) and heated to 120°C. To this, 350 g of inulin (Frutafit®) are added in a number of batches. The rotational speed of the kneader is 100 rpm, and the mixture is kept at 120–135°C for 20 minutes.

15 The mixture has a very low viscosity and as a result is readily processed as a glue. Upon cooling it sticks within a few seconds. It glues paper–paper, paper–glass, sheet–sheet/textile/cardboard etc. Dionex® HPLC chromatography is used to establish that during the production no chain breakdown of the inulin chains is taking place.

Examples 6–15

20 Inulin (Frutafit®, average DP about 10), glycerol and/or another plasticiser/filler were kneaded as described in example 5 (20 min 100 rpm at 120–135°C); the amounts used are summarised in table 3. The tensile strength of sheets of paper and textile glued with the mixture obtained is also summarised in table 3. A tensile strength on paper of 6–8 N/m² corresponds to tearing of the paper.

Example 16

25 Carboxylated inulin produced according to example 3 was suspended in water to a concentration of 81%. The suspension was tested directly according to example 4. The tensile strength of a glued layer (peeling experiments and tensile testing) was between 3 and 4 N/m² in case of paper on paper, and between 10 and 14 N/m² in case of textile on textile.

Table 3: Tensile strength on paper and textile

Example	inulin (g)	glycerol (g)	other ^a (g)	strength paper	strength textile
5	350	100	–	6–8	18–23
6	350	68	–	6–8	18–23
7	269	177	–	6–8	18–23
8	200	–	ur 200	4–5	15–18
9	200	100	ur 100	4–5	15–18
10	300	150	lac 50	6–8	18–23
11	200	150	lac 150	6–8	18–23
12	300	150	lm 50	6–8	18–23
13	200	150	lm 150	6–8	18–23
14	350 ^b	97	–	6–8	18–23
15	350 ^c	97	–	6–8	18–23

^a : ur = urea; lac = lactose; lm = lime (Ca(OH)₂)

^b : inulin having an average DP of 5

^c : inulin having DP's of 3–5 (Actilight®)

Claims

1. Use of a fructan or a derivative thereof as a glue.
2. Use according to Claim 1, wherein a solution or dispersion of 10–80 wt.% of inulin is used.
- 5 3. Use according to Claim 1, wherein a solution or dispersion of 20–50 wt.% of inulin in water is used.
4. Use according to Claim 1, wherein a solution or dispersion of 10–60 wt.% of an oxidised or reduced inulin in water is used.
5. Use according to Claim 4, wherein said oxidised inulin is dialdehyde inulin or
10 carboxylated inulin having a degree of oxidation of 0.1–100%, in particular 1–60%.
6. Use according to Claim 1, wherein a solution or dispersion of 40–95 wt.%, in particular 60–90 wt.%, of fructan or derivative thereof in a polyol having a temperature of 60–160°C, in particular of 80–140°C, is used.
7. Use according to any one of the preceding claims for gluing paper, paper-
15 containing products, wallpaper, textile, plastic products, wood, wood-containing products or cellulose-containing products.
8. Solution or dispersion of 40–95 wt.% of fructan or derivative thereof in a polyol.
9. Process for producing a solution or dispersion suitable as an adhesive,
20 comprising heating a mixture of 10–99 wt.% of a fructan or derivative thereof and 1–90 wt.% of a polyol and optional additives at a temperature of 80–160°C, in particular at 110–140°C.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,19 05 054 (DIERKS FORESTS INC.) 21 August 1969 see claims -----	1,7

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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